# Studies on the Equilibrium between the Dilute Solution and Solute Vapour. II.[1]

By Ituro UHARA.

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## Part III. Factors Affecting the Condensation Coefficient ($\alpha$) of Solute Vapour.

(9) *Relations between $\alpha$ and some physical properties of solvents* (L). No direct parallelism between $\alpha$ of iodine and some physical constants of L, surface tension $\sigma$, internal pressure, solubility, thermal conductivity (rapid vanishing of the heat of adsorption at the liquid surface was supposed to prevent re-evaporation of a solute molecule and to result in the increase of $\alpha$) and the diffusion coefficient of iodine is not observed.

The potential difference measured by Frumkin(*) for aqueous solutions (or the estimated values from his data) is given in Table 7 and 8. This is governed by the orientation of water or adsorbed molecules and the distribution of ions near the surface. $\alpha$ of iodine seems to be entirely independent of its sign and magnitude. Though $\alpha$ of methanol (dipole moment$=1.68\times10^{-18}$ e.s.u.) is given below, the result of an analysis of a minute amount of it is not exact enough to decide whether the observed effects are true or not.

| L | $H_2O$ | $MgSO_4$ 1 mol. aqueous solution | $i$-$C_4H_9CO_2H$ 0.11 mol. aqueous solution |
|---|---|---|---|
| Surface potential difference (mv.) | — | +3 | +300 |
| ($\alpha$ at 15°C.) $10^4$ | 6.2 | 7 | 8 |

(10) *Addition of electrolytes.*

Table 7. $\alpha$ of $I_2$ for Aqueous Solutions of Electrolytes. (See Fig. 8.)

| Electrolyte | $MgSO_4$ | $KNO_3$ | | $H_2SO_4$ | | |
|---|---|---|---|---|---|---|
| Conc. mol./l. | 1 | 1 | | 0.5 | 0.05 | 0.005 |
| $t$°C. | 25 | 25 | 12 | 22 | 21.7 | 20 |
| $\alpha/(\alpha$ for $H_2O)$ | 0.58 | 0.92 | 1.0 | 0.60 | 0.80 | 0.94 |
| Ratio of solubility of $I_2$ | 0.47 | 0.872 | | | 1.01 | |
| Surface potential in mv. | +3 | −ca. 10 | | −7 | | |
| $\Delta\sigma$ dyne/cm. | +2.49 | 0.816 | | 0.234 | | |

(1) I. Uhara, this Bulletin, **18**(1943), 412.

* See (9) in the preceding paper, *loc. cit.*

Ions are repelled from the liquid surface by the image force or large interaction with water. According to S. OKA[2], the distribution of ions near the surface of an aqueous solution (0.05 mol./l.) of 1–1 type electrolyte is as follows:

| Distance from surface (A) | 0 | 0.5 | 1 | 2 | 5 | 20 |
|---|---|---|---|---|---|---|
| Conc./conc. of bulk solution | 0.0 | 0.0 | 0.05 | 0.26 | 0.71 | 0.99 |

The layer of pure water at the surface of a salt solution is concluded to be 3.3–4.2 A thick (monomolecular) from the increase of $\sigma$.[3] Therefore, mere collision of an iodine molecule with a surface does not lead to the chemical reaction with ions in the solution. As the negative adsorption of ions takes place very rapidly, the obtained $\alpha$ is that for normal surface. In the aqueous solution of electrolyte and non-electrolyte, due to the electric field around ions, the component of a higher dielectric constant (water) is pulled preferentially into the field and the one of a lower dielectric constant (non-electrolyte) is forced out.[4] The same repulsion may act on S molecules at the surface, decreasing $\alpha$. Ions with many charges have large effect at equal distance, but as they exist deep in the liquid, the influence on $\alpha$ is not simply predicted.

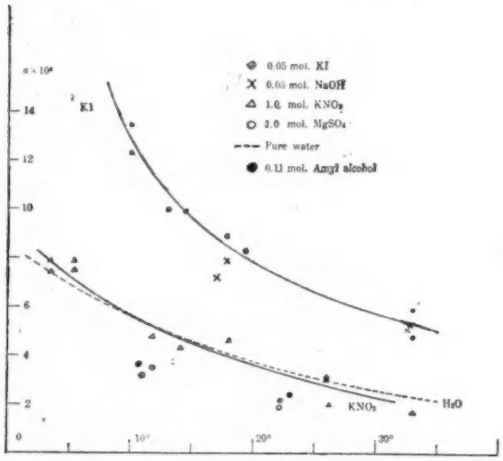


Fig. 8. α of Iodine on aqueous solution.

(11) *The case where chemical reaction takes place between the solute and the solvent.*

(2) *Proc. Physi.-Math. Soc. Japan*, **14**(1932), 656.
(3) Langmuir, *J. Am. Chem. Soc.*, **39**(1917), 1897.
(4) Theory of salting-out effect by Debye, *Z. physik. Chem.*, **130**(1927), 56.

Table 8. $\alpha$ for Aqueous Solutions of Electrolytes Which React with S. $S = I_2$.

| Electrolytes | NaCl(5) | HCl | | | KI (Fig. 8) | | | NaOH(6) | | KOH |
|---|---|---|---|---|---|---|---|---|---|---|
| Conc. mol./l. | 1 | 1 | 0.05 | 0.001 | 0.05 | | | 1 | 0.05 | 0.01 |
| $t$°C. | 20 | 17.2 | 18.2 | 18.2 | 25 | 15 | 10 | 20 | 20 | 16.3 |
| $\alpha/(\alpha$ for $H_2O)$ | 1.50 | 1.13 | 1.28 | 0.98 | 2.25 | 2.10 | 2.09 | 1.55 | 1.91 | 3.01 |
| Ratio of solubility of $I_2$ | 1.70 | 2.76 | 1.09 | 1.00 | 19.3 | | | | | |
| Surface potential (mv.) | −1 | −23 | | | −2 | | | +0 | | + |

| | S = HCl | | S = $NH_3$ | |
|---|---|---|---|---|
| L | $H_2O$ | 0.05 N NaOH aq. | $H_2O$ | 0.5 N HCl aq. |
| $t$°C. | 28.4 | 29 | 16 | 15 |
| $\alpha \times 10^4$ | 1.89 | 1.67 | 48 | 49.5 (by alkalimetry) |
| $\alpha(/\alpha$ for $H_2O)$ | | 0.88 | | 1.03 |

When the solution contains the electrolytes which can combine with iodine, perhaps iodine molecules vibrating in an adsorbed state at the surface have a chance to combine with them before re-evaporation, as ions exist only in the interior of the liquid. As the counter influence of ionic charge becomes effective with the concentration of electrolyte, more concentrated solutions do not necessarily show higher values of $\alpha$. The absorption velocity of ammonia by water and acid is the highest value obtained, probably due to its ability to combine with water molecules at the surface (immersion in liquid is not necessary in these cases).

Small value of hydrogen chloride compared with equally high solubility in water (750 c.c. of ammonia, 451 c.c. of hydrogen chloride in 1 c.c. of water at 18°C. is explained as follows: the hydrogen chloride molecule itself shows no large affinity (Van der Waals' $a$ is small) to water and it is only after the dissolution and ionization into $H_3O^+ + Cl^-$ that its high affinity to water is observed. The action of alkali is also for $H_3O^+$ and not for hydrogen chloride, hence no accerelating action is observed, as $\alpha$ is related to the phenomena before the dissolution. Ionization, however, shows some analogous effect to that of chemical reaction on $\alpha$, and $\alpha$ of hydrogen chloride for water is considerably larger than those for various non-ionizing L (Table 1.). It depends on the difference in mechanism that the effect of reactable substances in solution on $\alpha$ is far less than in the case of ordinary absorption under bubbling or stirring (§ 13).

Next, the eqilibrium of $I_3^-$ in 0.05 N potassium iodide aqueous solution (25°C) is discussed. $I^- + I_2 = I_3^- + 13.2$ kcal., $(I^-)(I_2) = (I_3^-)$ 0.00136. The solution dissolves $25.77 \times 10^{-3}$ mol./l. $I_2$ and the composition of this mixture is $(I^-)$ $25.65 \times 10^{-3}$, $(I_2)$ $1.42 \times 10^{-3}$, $(I_3^-)$ $24.35 \times 10^{-3}$ mol./l. $\alpha$ of iodine for 0.05 N potassium iodide aqueous solution and water are $7.0 \times 10^{-4}$ and

(5) Formation of $ClI_2^-$ is proved from partition coefficient determination. Rây and Sarkar, *J. Chem. Soc.*, **121** (1922), 1449.

(6) For the analysis of $I_2$, the contact with organic substances must be avoided.

$3.11 \times 10^{-4}$, and this difference is attributed to the above-mentioned reaction (the repulsion effect is negligible owing to the low concentration). As about half of $I^-$ is left uncombined in the mixture and can catch iodine molecules at the surface, we may assume that $a$ equals $4.8 \times 10^{-4}$ for this mixture. For the equilibrium of the vapour and the solution, we can write, assuming $\beta_1$ and $W$ of iodine are the same as in pure water,

$$ap\,10^3/RT = (\beta_1 C\sqrt{M/M'}\,e^{-W/RT})_{I_2} + (\beta_1 C\sqrt{M/M'}\,e^{-W/RT})_{I_3^-}$$

$$8.0\times10^{-9} = 5.56\times10^{-9} + 1.12\times10^{-11} \qquad \therefore\ \beta_1 \text{ of } I_3^- = 220\,,$$

from $$\beta_1 = \beta_2\left\{1+2\frac{W}{RT}+\frac{1}{2}\left(\frac{W}{RT}\right)^2\right\}, \qquad \beta_2 = 0.76\,. \quad \text{(See § 6.)}$$

(12) *Influence of surface active substances.*

Table 9. $a$ of $I_2$ for Aqueous Solutions of Surface Active Substances.

| | $C_2H_5OH$ | | $C_5H_{11}OH$ | | *sec*-$C_8H_{17}OH$ | $C_9H_{19}CO_2H$ | $C_{17}H_{35}CO_2Na$ |
|---|---|---|---|---|---|---|---|
| 1/(mol.fraction) | 3 | 500 | 500 | | $10^4$ | $>10^5$ | 15000 (new solution) |
| $t$°C. | 33.3 | 23.3 | 23.0 | 10.7 | 22.1 | 33.0 | 24.0 |
| $\frac{a}{a \text{ for } H_2O \text{ at } t°C.}$ | 1.39 | 1.07 | 0.72 | 0.67 | 0.45 | 0.73 | 0.25 |
| $\frac{a \text{ for pure org. subst.}}{a \text{ on } H_2O \text{ at } 20°C.}$ | 1.19 | | 1.7 | | | | |
| Surface potential (mv.) | +370 | | +250 | | +ca. 50 | +70 | −30 |

Rough parallelism is seen between $(a$ for water$)/a$ and following quantity: (quantity at the surface) × (length of alkyl radical) $\propto\left(-\frac{d\sigma}{dC}\right)\times$ (Conc.) × (the number of C in alkyl). That the mere existence of alkyl at the surface cannot be the cause of the decrease of $a$ is apparent from higher $a$ of pure hydrocarbons and higher alcohols or the aqueous solution of ethanol. A higher alcohol molecule at the water surface lies flat like a rod, with one side exposed in the air (§ 8). It may be supposed that iodine molecules colliding with the part are adsorbed less firmly than those colliding with smooth water surface, therefore such a diminution of effective area for dissolution results in the decrease of $a$. Considerable depression of $a$ (not due to reducing impurities as were ascertained by the blank test) shows the existence of these solutes in a considerable amount at the surface in spite of the short time (under 0.01 sec.) that the liquid from the point of thin glass tube contacts with the vapour.

For *sec*-octyl alcohol solution, concentration=3 molecules in $(100\,A)^3$. $a$ is 45% of water, and then if assumed that about half of the surface of water is covered by these molecules (about 50 $A^2$ per molecule when it lies) 100 molecules per $(100\,A)^2$ are necessary, which is the quantity contained in the solution of 3000 A thick. As there is almost no concentration gradient in the solution, it is unable to bring this amount to the surface by diffusion in 1/200 sec., and $\sigma$ of newly formed surface of

the aqueous solution of surface active substances requires time 0.01–1.0 sec, sometimes over a few minutes till it shows a constant value, indicating the slowness of diffusion. According to the measurement of $\sigma$ by the vibrating-jet method, the soap solution[7] of the same concentration used in our experiments shows the same value as water (the surface is about 0.01 sec. old), while the static method gives a value which is only 47% of that of water. This descrepancy may be explained by the following assumption: S is concentrated near the glass wall then flows down as in Fig. 9(a), stream lines being kept undisturbed (as the liquid in direct contact with the wall does not move, this adsorption must be multi-molecular)[8]. The suspension of powdered glass in water increased its stability on adding minute quantity of amyl alcohol, presumably favouring the foregoing assumption. In the dynamical method of $\sigma$ measurement, stream lines are disturbed and the stirring of a solution takes place. (Fig. 9 b, c).

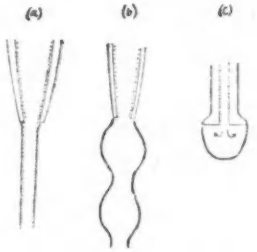

Fig. 9.

(13) *Relation between $\alpha$ and ordinary absorption velocity ($V$) of gas or vapour.* When acetone vapour of low pressure is sent on water surface stirred (170 r.p.m.) values $2.2–3.3 \times 10^{-5}$ are obtained as $\alpha$, while real value is far larger, $4.4 \times 10^{-4}$. In ordinary absorption, S accumulates near the liquid surface owing to slow diffusion in liquid, and re-evaporation takes place in consequence of partial pressure determined by Henry's law, hence $V$ increases remarkably with solubility, while $\alpha$, being governed by conditions of the first step of dissolution, is of the same order of magnitude for one solute, no parallelism with solubility observed. Condensation coefficient ($\alpha'$) calculated from the results of some bubbling methods convenient to measure initial velocity ($V_0$) of absorption is compared with $\alpha$ by the author's method.

| | $V_0$ c.c./sq. cm. min. | $\alpha'$ | $\alpha$ |
|---|---|---|---|
| HCl into $H_2O$ | 54.30[9] | $0.91\times10^{-4}$ (22°C.) | $1.89\times10^{-4}$ (28.4°C.) |
| $NH_3$ into $H_2O$ | ca. 1800[10] | $20\times10^{-4}$ | $48\times10^{-4}$ (16°C.) |

Though about half values of $\alpha$ are obtained in these cases due to large solubility and little re-evaporation, $\alpha'$ will be far less than $\alpha$ for less soluble gases, therefore $\alpha$ cannot be obtained by bubbling or stirring methods.

*The effect of surface active impurity on absorption velocity of vapour.* Here also, the difference between $\alpha$ and $V$ is shown characteristically.

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(7) Rayleigh, *Proc. Roy. Soc.*, A, **47**(1890), 281.

(8) H. Akamatu, J. *Chem. Soc. Japan*, **17**(1942), 141, 161, 260, showed the existence of multi-molecular adsorption of lower fatty acid in benzene at the glass surface.

(9) Becker, *J. Ind. Eng. Chem.*, **16**(1924), 1223.

(10) Ledig and Weaver, *J. Am. Chem. Soc.*, **46**(1924), 650.

Table 10. Comparison between $a$ and $V$ on Aqueous Solution at Rest. $S = I_2$.

| Impurity | Fat | $C_5H_{11}OH$ | *sec*-$C_8H_{17}OH$ | $C_{17}H_{35}CO_2Na$ (new solution) | | |
|---|---|---|---|---|---|---|
| 1/(mol. fraction) | monolayer | 500 | $10^4$ | $1.5\times10^4$ | $10^5$ | $2\times10^5$ |
| $a$/($a$ for $H_2O$) | — | 0.70 | 0.45 | 0.25 | | 0.78 |
| $V$/($V$ for $H_2O$) | 1.0 | 1.9 | 2.4 | | 0.63 | |

It is quite natural that a fat layer has no effect on $V$, because the difusion velocity of iodine accumulated in the liquid near the surface is rate-determining. In an aqueous solution of a higher alcohol, the surface concentration is far higher than that of bulk solution (§ 8), and as this portion of the solution shows larger solubility than water for iodine, diffusion becomes faster by larger concentration gradient towards the interior. Effects on $a$ and $V$ are entirely reversed due to the difference in mechanism. Soap in solution is ionic and does not increase solubility of iodine, and moreover the space for iodine may be greatly diminished owing to remarkable adsorption and large molecular dimension.

$V$ measured under stirring or flowing liquid is intermediate between two extreme cases above-mentioned.

Riou[11] and others stated that the velocity of absorption of carbon dioxide by flowing sodium carbonate solution is increased by the addition of substances which depress $a$, but this does not coincide with our results for soap solution. In general, it may be concluded as follows:

(a) When liquid surface is renewed very quickly and the pressure of S is low (seldom met in practice), $V$ is determined by $a$. A large molecule of strong surface activity depresses $V$.

(b) In most usual cases in which diffusion velocity at the surface is rate-determining, addition of a substance which increases solubility of a solute (with more solubility for S than water and it is better if it is surface active) is effective to increase $V$, e.g. methanol dissolves four times of carbon dioxide than water and addition of 2% methanol in sodium carbonate aqueous solution can increase $V$ of carbon dioxide by 20%. Viscosity has no direct relation with $V$.[11]

*The effect of surface active impurity on evaporation of the solute.* The evaporation velocity of iodine from aqueous solution is almost unaffected by addition of amyl alcohol, as the partial pressure of iodine is unchanged though its concentration is increased at the surface. To prevent evaporation of S, substances which can cover the surface without increasing solubility of S must be added.

(14) *The influence of T.* The existence of potential barrier at the interface of gas and liquid may be supposed from small values of $a$, which results in the increase of $a$ with rising $T$, $(da/dT>O)$, and the same conclusion is also drawn out from a simple model of dissolution mechanism that the gap among liquid molecules at the surface is broadened with

(11) *Compt. rend.*, **174**(1922), 1017, 1463; **184**(1927), 325; **186**(1928), 1543, 1727; Killeffer, *J. Ind. Eng. Chem.*, **29**(1937), 1293.

rising $T$. As a matter of fact (§ 4), however, $a$ decreases considerably with $T$, and log $a$ and $1/T$ are related linearly to data with comparatively high accuracy, hence

$$a = D\,e^{+A/RT} \qquad (14)$$

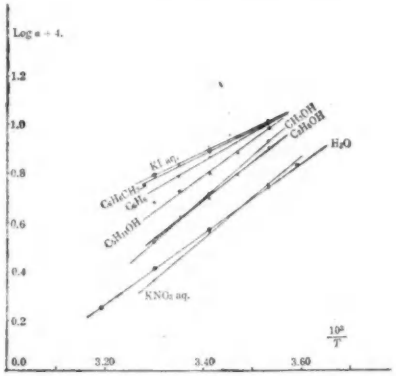


Fig. 10. The temperature dependence of $a$ of iodine on various solvents.

Table 11. $S = I_2$. $W$ = Heat of Solution of Vapour.

| L | $A$ $\frac{\text{kcal.}}{\text{mol.}}$ | $A/W$ | $D$ |
|---|---|---|---|
| $H_2O$ | 6.54 | 0.68 | $4.86\times10^{-9}$ |
| 1N $KNO_3$ aq. | 7.66 | — | $7.04\times10^{-10}$ |
| 0.05N KI aq. | 4.31 | — | $4.68\times10^{-7}$ |
| $C_2H_5OH$ | 7.11 | 0.54 | $2.48\times10^{-9}$ |
| $CH_3OH$ | 8.02 | 0.62 | $5.26\times10^{-10}$ |
| $C_5H_{11}OH$ | 6.61 | — | $7.36\times10^{-9}$ |
| $C_6H_5CH_3$ | 4.48 | 0.48 | $3.68\times10^{-7}$ |

## Summary.

(1) Various factors affecting condensation coefficient of solute vapour on the liquid surface of solvents (chiefly $a$ of $I_2$) were studied.

(2) $a$ has no parallelism with many physical quantities of solvents (surface tension, solubility etc.).

(3) Effects of addition of electrolytes, surface active non-electrolytes, reactable substances were discussed.

(4) $a$ decreases with rising temperature.

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# Studies on Nickel and Cobalt in Arsenopyrites. I. Estimation and Determination of Cobalt in Some Arsenopyrites.

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The studies on cobalt in arsenopyrites have been tried by many of the mineralogists and geochemists. For example, in Doelter's handbook[1] we can find a number of the analytical results. However, owing to the lack of sensitivity in the methods, these investigators were not able to determine a minute quantity of cobalt, the minimum of cobalt determined being about 0.05% in almost all the cases. On the other hand recent investigations show that some of the arsenopyrites containing a fair amount of cobalt include crystals of other cobalt-rich minerals as small as possible to be found under microscope. Even those containing a smaller amount of cobalt sometimes include such cobalt-rich minerals.

However, there are pure arsenopyrites without inclusion of other minerals but with some amount of cobalt that replaces iron therein. To see if all of the arsenopyrites contain cobalt is the main purpose of the present investigation and obviously it would be attained by applying a most sensitive analytical method. Choosing and examining the nitroso-R-salt method, the author succeeded in estimating a minute quantity of cobalt. The result will be briefly reported in the present paper.

## Preliminary Investigation on the Nitroso-R-salt Method.

Nitroso-R-salt was at first employed by H. S. van Klooster[2] as the reagent for the detection of cobalt, and next by F. J. Stare and C. A. Elvehjem[3] for the quantitative analysis of cobalt in animal nutrition. Afterwards the method by the latter investigators was modified by E. B. Kidson *et al.*[4], and recently more improved by H. T. Macpherson and J. Stewart[5]. Annie M. M. Davidson and R. W. Mitchell[6] also used the method similar to that of Macpherson and Stewart but independently of them.

This method depends on the development of red-coloured complex of nitroso-R-salt and cobalt, the intensity of the colour being proportional to the amount of cobalt present. The recent investigators used a Pulfrich photometer to measure the final colour and Kidson claims to have obtained

(1) C. Doelter and H. Leitmeier, "Handbuch der Mineralchemie", Dresden and Leipzig (1926).

(2) H. S. van Klooster, *J. Am. Chem. Soc.*, **43**(1921), 746.

(3) F. J. Stare and C. A. Elvehjem, *J. Biol. Chem.*, **99**(1933), 473.

(4) E. B. Kidson, H. O. Askew and J. K. Dixon, *New Zealand J. Sci. Tech.*, **18** (1936), 601.

(5) H. T. Macpherson and J. Stewart, *Biochem. J.*, **32**(1938), 763.

(6) Annie M. M. Davidson and R. L. Mitchell, *J. Soc. Chem. Ind.*, **59**(1940), 232.

reproducible results with as little as 0.0001 mg. cobalt by using a blue filter (S47) of the photometer. Macpherson and his collaborator, however, report that readings obtained by the blue filter depend on the quantity of iron present and therefore are of no value in estimating the cobalt in the solution not free from iron. Substituting the blue filter by a green one (S53), they obtained constant readings for a particular cobalt solution, no matter what quantity of iron present. The author tried again to use both of the filters and attained the same results as those of Macpherson.

However, as the amount of iron becomes greater, some interference due to iron appears even in the case when the green filter is employed. This interference was thoroughly investigated in the present study, because the present intention is to determine cobalt in arsenopyrites containing a great amount of iron. The interference due to manganese also was taken into consideration and thoroughly investigated, though Macpherson says that manganese did not interfere, even in very large amount.

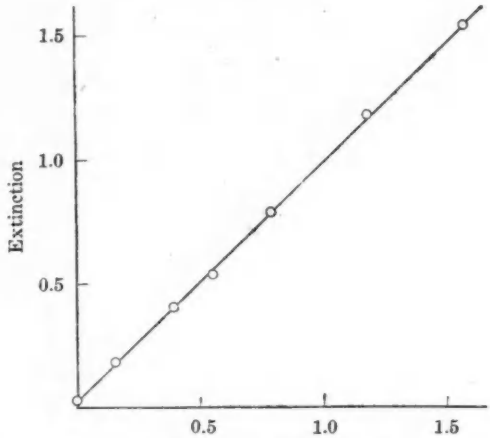
Removal of iron with ether as described by Kidson *et al.* and by Davidson and Mitchell was carried out to retain the blue filter, since it gave considerably higher readings than the green. The writer found it unsatisfactory as did Macpherson, since iron was not removed completely even after several washings. By the precipitation with ammonium hydroxide in the presence of an excess of ammonium chloride and by the basic acetate method the separation of cobalt from iron was not satisfactory. At last the precipitation by means of zinc oxide[5] was tried, by which Macpherson found a very satisfactory results. The method was examined using the cobalt solution containing various amounts of iron. The results will be described together in the following.

*Reagents Required.*

Hydrochloric acid: N/2 and sp. gr. 1.12 (7.3 N).
Nitric acid: 1.1.
Potassium hydroxide: 10% aqueous solution.
Sodium acetate (guaranteed).
Zinc oxide (guaranteed).
Nitroso-R-salt: 0.1% aqueous solution.
Phenolphthalein: 0.2% alcoholic solution.

*Procedure.* (a) Colour development. Taking the solution to be determined, treat it with 0.5 c.c. of hydrochloric acid (sp. gr. 1.12) and 6 drops of nitric acid (1:1). Make the solution up to 15 c.c., boil for a few minutes to oxidize any reducing substances, and then cool. Add first 2 c.c. of 0.1% solution of nitroso-R-salt, then 2 g. of sodium acetate, and heat the mixture to 70°C. Add 5 drops of phenolphthalein and then 10% potassium hydroxide drop by drop, until a pink colour develops. Now add 3 more drops of phenolphthalein and 0.5 N hydrochloric acid enough to destroy the pink colour. Boil for 120 seconds, then add 5 c.c. of nitric acid (1:1). Continue boiling for a further 120 seconds. Cool the solution under tap, make up to 50 c.c. in a volumetric flask, and filter the solution through a fine-grain paper.

(b) Photometric determination. Find the extinction coefficient by means of the Pulfrich photometer, using filter S53 and the 50 mm. cell, with distilled water in the compensating cell. The cobalt present is then found from the standard graph (Fig. 1), which is made by plotting the figures obtained using the cobalt standard solutions.




Filter: S 53 Cell: 50 mm.

Fig. 1.

This standard solution was assured to contain neither iron nor nickel. The mean error for the determinations of cobalt standard solution did not exceed 2% as shown in Table 1.

Table 1.

| Co present (p.p.m.) | Scale readings | Co found (p.p.m.) | Error (p.p.m.) |
|---|---|---|---|
| 0.158 | 0.182 | 0.160 | +0.002 |
| 0.158 | 0.182 | 0.160 | +0.002 |
| 0.395 | 0.394 | 0.383 | −0.012 |
| 0.395 | 0.405 | 0.395 | 0.000 |
| 0.553 | 0.535 | 0.531 | −0.022 |
| 0.553 | 0.529 | 0.525 | −0.028 |

Table 1.—(*Continued*)

| Co present (p.p.m.) | Scale readings | Co found (p.p.m.) | Error (p.p.m.) |
|---|---|---|---|
| 0.790 | 0.784 | 0.791 | +0.001 |
| 0.790 | 0.784 | 0.791 | +0.001 |
| 1.185 | 1.160 | 1.186 | +0.001 |
| 1.185 | 1.173 | 1.201 | +0.016 |
| 1.580 | 1.530 | 1.575 | −0.005 |
| 1.580 | 1.520 | 1.564 | −0.016 |

*Interference of Iron Present and Use of Zinc Oxide.* As described before, when a greater amount of iron is present in the solution to be determined some interference appears, which is shown clearly in the figures given in Table 2. The sample solution was prepared by combining the standard solutions of cobalt and iron, the latter of which also contains neither cobalt nor nickel as examined by an x-ray spectroscopy. Sometimes, especially when a large amount of iron was required to be

added into the solution, solid ferric chloride ($FeCl_3 \cdot 6H_2O$) was substituted for the iron standard solution, after being assured to contain a negligible amount, if any, of cobalt.

As a result, the presence of iron did not give reproducible results, the variable readings being obtained even when the same amount of iron is present. When the same amount of cobalt is taken, in general, the greater the amount of iron, the smaller is the extinction coefficient. The reason would be in the following fact: During the neutralization with potassium hydroxide, a precipitate is formed due to the iron in the solution. This may interfere with the adjustment of the reaction and leave the unreacted cobalt after the precipitate has disappeared on addition of the concentrated nitric acid.

Therefore, it is obvious that iron must be removed if the sample contains a large amount of it. As described above, the best results were found in precipitation by means of zinc oxide with the procedure as shown in the following.

Table 2.

| Co present (γ) | Fe added (mg.) | Co found (γ) | Co found (%) |
|---|---|---|---|
| 39.5 | 4.55 | 37.7 | 95 |
| 39.5 | 9.10 | 40.5 | 102 |
| 39.5 | 17.2 | 35.0 | 89 |
| 39.5 | 22.75 | 38.5 | 97 |
| 39.5 | 34.4 | 35.7 | 90 |
| 39.5 | 45.5 | 39.1 | 99 |
| 39.5 | 68.8 | 28.7 | 73 |
| 39.5 | 103.2 | 24.8 | 63 |

Table 3.

| Co present (γ) | Fe added (mg.) | Co found (γ) | Co found (%) |
|---|---|---|---|
| 39.5 | 0 | 38.3 | 97.5 |
| 39.5 | 17.2 | 38.3 | 97.0 |
| 39.5 | 34.4 | 38.0 | 96.2 |
| 39.5 | 68.8 | 37.2 | 94.2 |
| 39.5 | 172.0 | 32.2 | 81.6 |
| 39.5 | 344.0 | 32.7 | 82.8 |

Prepare the solution by combining the standard solutions of cobalt and iron. Evaporate the contents almost to dryness, and take up the residue with 2 c.c. of hydrochloric acid (sp. gr. 1.12) and a little water. Make the volume of solution about 25 c.c., boil for 2 minutes and cool. Add a slight excess of an aqueous suspension of zinc oxide, boil for 1 minute and filter hot. Wash thoroughly with about 50 c.c. of hot water. Evaporate the filtrate and washings to about 15 c.c., add 0.5 c.c. of hydrochloric acid (sp. gr. 1.12) and 6 drops of nitric acid (1:1), boil for 2 minutes and proceed with the estimation of cobalt as directed above.

The results were shown in Table 3. From the figures in Table 3, it will be noted that the greater the amount of iron, the smaller is the cobalt content found. The relation is more clearly shown in Fig. 2. It may be dangerous to use this procedure as a most exact method for determining cobalt in the presence of a large amount of iron, because the deviation from the colour intensity developed in the solution free from iron is fairly large. Even the presence of 100 mg. of iron in the solution makes the colour intensity due to cobalt considerably smaller —about 92% cobalt of the original content.

For the purpose of estimating cobalt, however, the method, owing to its sensitivity, would have a possibility of being safely used. Moreover,

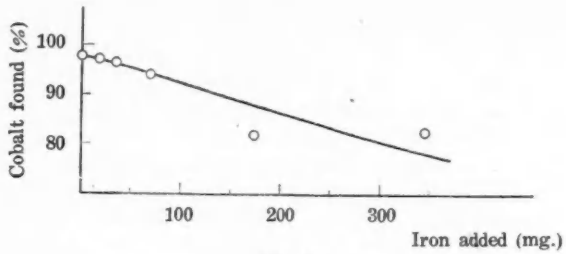



Fig. 2.

if the sample solution is adjusted as containing iron less than 50 mg. the error becomes smaller. The presence of 50 mg. iron makes the colour intensity of the final solution about 96% of that calculated from the cobalt present. The error would be admitted as trifling in the case when such a minute quantity is determined, nay, the method would be the most excellent for determining cobalt in the sample containing such an amount of iron.

*Interference of Manganese Present.* As described above, Macpherson says in his report that manganese did not interfere, even in a large amount. The author's first trial on the determination of cobalt in the presence of manganese showed that the cobalt content found is far less than that added. The somewhat systematic investigation, therefore, was carried out as follows. The sample solution was prepared by using the cobalt standard solution and manganese chloride ($MnCl_2 \cdot 4H_2O$), and the cobalt was determined in the way as directed above. The results are as given in Table 4. By addition of the nitroso-R-salt reagent and sodium

Table 4.

| Co present (γ) | Mn added (mg.) | Co found (γ) | Co found (%) |
|---|---|---|---|
| 39.5 | 25.9 | 33.1 | 84 |
| 39.5 | 25.9 | 36.2 | 92 |
| 39.5 | 42.8 | 31.8 | 81 |
| 39.5 | 42.8 | 32.2 | 82 |
| 39.5 | 58.7 | 18.0 | 46 |
| 39.5 | 68.9 | 17.7 | 45 |
| 39.5 | 86.5 | 21.5 | 54 |
| 39.5 | 86.5 | 28.1 | 71 |

Table 4.—(*Continued*)

| Co present (γ) | Mn added (mg.) | Co found (γ) | Co found (%) |
|---|---|---|---|
| 39.5 | 110.6 | 21.9 | 55 |
| 39.5 | 111.8 | 14.1 | 36 |
| 39.5 | 139.8 | 8.8 | 22 |
| 39.5 | 139.8 | 12.7 | 32 |
| 39.5 | 224.3 | 3.5 | 9 |
| 39.5 | 224.3 | 5.1 | 13 |
| 39.5 | 279.9 | 2.5 | 6 |
| 39.5 | 279.9 | 1.4 | 4 |

acetate, a green colour develops in the solution, which is perhaps due to a complex of manganese and the reagent. During the addition of potassium hydroxide, a white-coloured precipitate appears gradually, which is considered to be manganese hydroxide. The precipitation seems to begin when the solution shows somewhat greater pH than that shown when ferric hydroxide precipitates. The figures given in Table 4 were plotted as shown in Fig. 3, and these figures show the following facts.

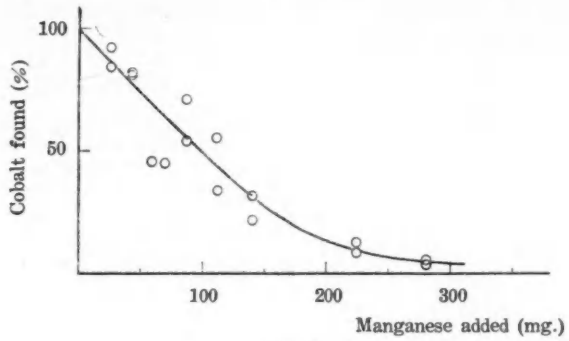



Fig. 3.

First, as the amount of manganese increases, the percentage of cobalt found decreases. Secondly, the method loses such a reproducibility as seen in the determination of cobalt only. The curve in Fig. 3 tells us the first fact clearly, and the second fact is evidently explained by the scattering of plotting points above and below the curve. At any rate, the interference due to manganese is far greater than that due to iron, and it is too great to be available for the determination.

It would be difficult to see why manganese interferes so much, because the theoretical treatment is almost impossible owing to insufficient knowledge of the reaction mechanism between cobalt and nitroso-R-salt. The following facts, however, give something suggestive to interpret the matter. Even if the addition of manganese is made after the reaction between cobalt and nitroso-R-salt, by treating with first potassium hydroxide and then hydrochloric acid, is over, it makes the content of cobalt found far less than that of cobalt added. Even manganese added after the boiling with nitric acid (1:1) interferes with the determination. From these facts, as summarized in Table 5, it is found that the interference of manganese present is not only due to the co-precipitation by manganese hydroxide, but also to the reaction itself between manganese and nitroso-R-salt, though most of it depends on the former. The interpretation was supported also by the attempts described in the following.

Table 5.

| Co present (γ) | Mn added (mg.) | Co found (γ) | Co found (%) | Note |
|---|---|---|---|---|
| 39.5 | 222.7 | 36.9 | 93 | (1) |
| 39.5 | 222.7 | 36.8 | 93 | (2) |
| 39.5 | 222.7 | 35.4 | 90 | (3) |

(1) Manganese was added immediately after the solution had been made acidic with 0.5N hydrochloric acid.
(2) Manganese was added after boiling without nitric acid for 120 seconds.
(3) Manganese was added after boiling with nitric acid for 120 seconds.

With the intention of using the method in the presence of manganese, some attempts were made, one of which is to see whether the change of time of the final heating can recover the lost amount of cobalt. This was unsuccessful as shown in Table 6; either an increase or decrease of the time of the final heating did nothing to retain the determination

method. The second attempt is to see whether the interference of manganese can be eliminated by adding a large amount of the nitroso-R-salt reagent. As recognized by Stare and Elvehjem in the case of a large amount of nickel present this alteration gave a fairly satisfactory result as shown in Table 7, though they said nothing of an influence of manganese present. Instead of 2 c.c. of nitroso-R-salt reagent 10 c.c. was added. A standard graph was made again, because the colour intensity due to the reagent only increases as much as five times. As represented in the first line of Table 7, the presence of 70.9 mg. of manganese gives almost no influence to the determination; 99.0% of the cobalt added was found, instead of about 63% in the case of using 2 c.c. of the reagent. As a result, the method can be employed in the presence of a fairly large amount of manganese, although they accuracy in the determination, especially when the amount of cobalt is very minute, lessens to some extent.

Table 6.

| Co present (γ) | Mn added (mg.) | Time of boiling with 1:1 $HNO_3$ (min.) | Co found (γ) | Co found (%) |
|---|---|---|---|---|
| 39.5 | 139.8 | 1 | 9.8 | 25 |
| 39.5 | 139.8 | 3 | 8.8 | 22 |
| 39.5 | 139.8 | 5 | 9.0 | 23 |
| 39.5 | 139.8 | 7 | 14.2 | 36 |
| 39.5 | 139.8 | 10 | 4.4 | 11 |

Table 7.

| Co present (γ) | Mn added (mg.) | Co found (γ) | Co found (%) |
|---|---|---|---|
| 39.5 | 70.9 | 39.0 | 99 |
| 39.5 | 137.2 | 33.8 | 86 |

## Cobalt Content of Some Arsenopyrites.

Cobalt in arsenopyrites was determined; some of it by gravimetry and others by colorimetry. When the determination was made, the arsenic present in the samples caused the analysis to be a tedious one. There are usually two methods for separating arsenic; one is by precipitation with hydrogen sulphide and the other by distillation. In the present study, the latter method was taken up, because the former tends to give an incomplete separation of arsenic from the sample solution. In general, it is difficult to precipitate arsenic completely with hydrogen sulphide. The conditions for making the precipitation complete are found in a rapid passage of the hydrogen sulphide gas into the hot concentrated hydrochloric acid solution. Even under such conditions the complete removal of arsenic is apt to fail. The distillation method, on the other hand, is convenient for the present purpose. Arsenic is reduced to arsenous in the presence of reducing reagent, such as cuprous chloride, ferrous sulphate or hydrazine sulphate, and distilled off by heating with hydrochloric acid with the concentration of about more than 9 N. The greater the concentration of the acid, the better is the distillation result. Therefore the acid should be added in several portions during the distillation. In the case of the distillation for the purpose of determining arsenic, cuprous chloride or ferrous sulphate is commonly used as the reducing reagent. In the present case, however, of separating arsenic for the purpose of determining a small amount of cobalt, such reducing reagents containing heavy metals are not convenient. As the presence of a large quantity of heavy metals interferes doubtlessly with the determination, we must

avoid using such reagents. From this point of view, hydrazine sulphate was taken up, which leaves no heavy metals that interfere with the determination.

To separate cobalt from iron, the latter element must be oxidized. In the presence of hydrazine sulphate it is not easily done, so an excess of hydrazine sulphate must be removed. Even by heating with nitric acid, the reagent was decomposed with difficulty, and its complete removal was hardly attained. This procedure, therefore, had to be given up. The second attempt was to precipitate iron, cobalt and others with hydrogen sulphide in an ammoniacal solution, leaving hydrazine sulphate in the filtrate. By this method hydrazine sulphate was removed completely from the precipitate containing iron, cobalt and others, without any loss of them. The procedure will be described later.

*Samples.*

The samples taken up in this study are as follows:—

(1) From the Hōrai mine, Yamanasi Prefecture.
(2) From Syarindō, Nanzan-men, Keizan-gun, Korea. No. 1.
(3) From Syarindō, Nanzan-men, Keizan-gun, Korea. No. 2.
(4) From Syarindō, Nanzan-men, Keizan-gun, Korea. No. 2'.
(5) From Tukuhara, Hikoma-mura, Aso-gun, Totigi Prefecture.
(6) From Tuyagawa, Ōtuho-mura, Higasi-iwai-gun, Iwate Prefecture.
(7) From the Taisi mine, Yahagi-mura, Kisen-gun, Iwate Prefecture.
(8) From the Nagasima mine, Ōi, Yena-gun, Gifu Prefecture.
(9) From Nakatugawa, Ōtaki-mura, Titibu-gun, Saitama Prefecture.
(10) From Suzurisima-mura, Minami-koma-gun, Yamanasi Prefecture.

*Determination Procedure.* (1) For gravimetric method: Decompose the sample with nitric acid on a water-bath and then with the mixture of nitric and hydrochloric acids. Continue the heating till the sample is completely dissolved. Evaporate the solution up to dryness and expel the nitric acid by repeating several times the evaporation with hydrochloric acid. Treat the residue with a few c.c. of hydrochloric acid, transfer the solution into an Elrenmayer flask using about 15 c.c. washings of the same acid, and add 1 g. of hydrazine sulphate. The concentration of the acid in the solution should be more than 9 N. Then cover the flask with a funnel and boil the contents over a direct fire. Arsenic in the sample solution, reduced to arsenous, is distilled off. When the volume of contents decreases down to about 10 c.c., and 5 c.c. more of hydrochloric acid and continue the distillation. The procedure, distillation and addition of the acid, must be repeated five times to remove the arsenic completely. Dilute to about 30 c.c. and filter the insoluble residue and the excess of hydrazine sulphate. Adjust pH of the solution to be about 0.5 N, treat with hydrogen sulphide, and filter the precipitate, if any. Treat the filtrate with hydrogen sulphide, then make it ammoniacal. Then iron and cobalt precipitate, accompanying like elements. To make the precipitation complete, pass hydrogen sulphide again, filter and dissolve the precipitate with dilute hydrochloric acid. Expel the hydrogen sulphide, filter off sulphur and oxidize ferrous iron to ferric with nitric acid. To separate cobalt from iron, treat with ammonium hydroxide in the presence of a large amount of ammonium chloride.

Repeat this treatment three times, and combine all the filtrates and washings. Using the combined solution, determine the cobalt by the $\alpha$-nitroso-$\beta$-naphthol method.

(2) For colorimetric method. The sample was treated in the same way as in the case of gravimetry—decomposed with nitric and hydrochloric acids, distilled with hydrochloric acid in the presence of hydrazine sulphate to remove arsenic, precipitated by hydrogen sulphide and dissolved with dilute hydrochloric acid. The solution obtained was made into a suitable volume, using a volumetric flask, and taking an aliquot of it the colorimetric determination was carried out by the nitroso-R-salt method. Zinc oxide method for separating cobalt from iron was omitted because the amount of iron was not so large. The procedure for the determination was, as described before, with 2 c.c. of nitroso-R-salt reagent.

Table 8.

| Sample No. | Locality | Co | Ni |
|---|---|---|---|
| 2 | Syarindō No. 1 | ++ | − |
| 3 | Syarindō No. 2 | ++ | − |
| 5 | Tukuhara | + | − |
| 6 | Tuyagawa | − | − |
| 7 | The Taisi mine | − | − |

\+ shows the presence of line.
− shows the absence of line.

*Analytical Results.* Prior to the chemical treatment, cobalt and nickel contents of some of the samples were estimated by the spectroscopic method. As shown in Table 8, cobalt was detected in three of these samples and nickel in none of them.

The samples were analyzed by gravimetric or colorimetric method, according to their cobalt contents. The results are shown in Table 9.

Table 9.

| Sample No. | Locality | Cobalt content (%) | Method |
|---|---|---|---|
| 1 | The Hōrai mine | 2.53 | gravimetric |
| 2 | Syarindō No. 1 | 2.69 | " |
| 3 | Syarindō No. 2 | 1.73 | " |
| 4 | Syarindō No. 2′ | 3.36 | " |
| 5 | Tukuhara | 0.051 | colorimetric |
| 6 | Tuyagawa | 0–0.0022 | " |
| 7 | Taisi mine | 0.013 | " |
| 8 | The Nagasima mine | 0–0.0054 | " |
| 9 | Nakatugawa | 0.14 | " |
| 10 | Suzurisima-mura | 0–0.0054 | " |

To examine these results obtained by the colorimetric method, the following trial was carried out. The cobalt standard solution containing 20–30 $\gamma$ of cobalt was added into the sample solution, and the content was determined, after being treated by the same procedure. If the method is accurate, the cobalt content obtained will be equal to the sum of cobalt contents of the original sample solution and the added cobalt standard solution. Sample from Tukuhara, Totigi Prefecture, (Sample No. 5) was

taken for this examination and a satisfactory result was obtained as shown in the following:

| | Sample No. | Weight of sample (mg.) | Cobalt added (γ) | Cobalt found (γ) |
|---|---|---|---|---|
| (A) | 5 | 48.66 | 0 | 24.7 |
| (B) | 5 | 48.66 | 19.7 | 43.8 |

"Cobalt found in (B)" is almost equal to the sum of "cobalt found in (A)" and "cobalt added". This fact shows that the determination method is very satisfactory, as it will be seen in the case of other samples also.

Nickel content of some of the sample was determined by colorimetric method[7] to see the ratio of cobalt to nickel. Four arsenopyrites containing a small amount of cobalt were chosen, because a great amount of cobalt interferes with the nickel determination owing to the colour of the complex of cobalt and dimethylglyoxime, which is similar to that of nickelic dimethylglyoxime. A large portion of cobalt in the sample can be removed by the extraction procedure, so the interference of cobalt, if its amount is small, is considered to be negligible. Both analytical results and the ratio of cobalt to nickel are shown in Table 10.

Table 10.

| Sample No. | Locality | Nickel content (%) | Atomic ratio Co/Ni |
|---|---|---|---|
| 7 | The Taisi mine | 0–0.0045 | more than 2.9 |
| 8 | The Nagasima mine | 0.012 | less than 4.5 |
| 9 | Nakatugawa | 0–0.0074 | more than 19 |
| 10 | Suzurisima-mura | 0.028 | less than 1.9 |

In conclusion it has become clear that all the smples analyzed contain a minute or fairly large quantity of cobalt. However, it is not yet found in what form cobalt is contained. The same matter comes up for question concerning nickel. To answer this problem a microscopic observation must be carried out, which will be taken up in the subsequent studies.

## Summary.

Nitroso-R-salt method has been investigated for the purpose of determining a minute quantity of cobalt in minerals. In some previous papers it was reported that the method is very satisfactory for determining cobalt in plants, soils and animal nutritions. In this study it has been proved that the method is also fairly satisfactory for determining cobalt in minerals containing a large amount of iron.

Cobalt content of some arsenopyrites has been determined by this colorimetric or the gravimetric method. The result shows that all the samples contain a minute or fairly large quantity of cobalt. However,

(7) N. Tanaka, this Bulletin, **18**(1943), 201.

the problem in what form cobalt is contained in these samples remains for the subsequent studies.

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